SOME DOUBLE SALTS

CONTAINING

SELENIUM

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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JAMES FLACK NORRIS

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Some Double Salts Containing Selenium.

INTRODUCTION.

A large number of double halides containing the aliphatic amines has been prepared. These show greater complexity than the double salts of ammonium or the alkali metals. Where all the possible combinations have been determined, the series of salts found are more complete, and a greater variety in composition is exhibited. For example, bismuth forms the following iodides[1] with dimethylamine: $2BiI_3.3(CH_3)_2NH.HI$, $3BiI_3.4(CH_3)_2NH.HI$, $3BiI_3.5(CH_3)_2NH.HI$. Copper has the complete series[2] $CuCl_2.(CH_3)_2NH.HCl$, $CuCl_2.2(CH_3)_2NH.HCl$, $CuCl_2.3(CH_3)_2NH.HCl$. And, finally, the following double chlorides of mercury[3] have been described: $5HgCl_2.(CH_3)_3N.HCl$, $2HgCl_2.(CH_3)_3N.HCl$, $HgCl_2.(CH_3)_3N.HCl$, $HgCl_2.2(CH_3)_3N.HCl$.

The general conclusion that the double halides containing the substituted ammonias are more complex than those containing ammonia and the alkali metals is strengthened by the results of the investigation of the selenium compounds. The influence of the introduction of alkyl groups on the stability of the halides of selenium is noticeable. Selenium tetrachloride is decomposed by water, and, even in the presence of strong hydrochloric acid, is not capable of entering into a double salt with ammonium chloride. Muthmann and Schäfer,[4] in their study of the double halides of selenium and ammonium, found that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.2H_2O$, in which there is a complete breaking down of the selenium tetrachloride.

The work on the compounds containing dimethyl- and trimethylamine brings out the fact that owing to the presence of

[1] Ann. Chem. (Liebig), **210**, 310.
[2] Jsb. d. Chem., 1883, 618.
[3] Jsb. d. Chem., 1883, 618.
[4] Ber. d. chem. Ges., **26**, 1008.

these bases, selenium can enter into combination as the oxychloride, $SeOCl_2$, where the molecule of the tetrachloride has undergone only half decomposition. The salts $SeOCl_2.(CH_3)_3N.HCl$ and $2SeOCl_2.3(CH_3)_2NH.HCl$ were obtained, when concentrated hydrochloric acid was the solvent. If the trimethylamine salt is recrystallized from dilute acid, one-half of the selenium oxychloride is changed into the oxide, and the salt $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$ is obtained.

Double salts containing selenium oxychloride are not unknown. Weber[1] prepared the following salts by mixing the oxychloride with the chlorides of the respective metals: $2SeOCl_2.SnCl_4$, $2SeOCl_2.TiCl_4$, $2SeOCl_2.SbCl_5$.

The bromides about to be described also show greater complexity than those containing ammonium. With ammonium bromide Muthmann and Schäfer succeeded in making the compound $SeBr_4.2NH_4Br$, while with both dimethyl- and trimethylamine three double bromides have been obtained.

The study of a salt containing selenium oxybromide, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, led to an interesting class of double salts containing selenium and a new base. An attempt was made to replace the oxygen in the above compound by crystallizing it from a solution containing a large quantity of free bromine. The salt $SeBr_4.(CH_3)_3N.HBr$ would thus result. This was not obtained, but a well characterized compound, which dissolved in water with evolution of bromine. Two explanations of the action of the bromine were possible: either the selenium, in the presence of such a strong oxidizing agent, entered into combination in the hexavalent state with the formation of the salt $SeBr_6.2(CH_3)_3N.HBr$, or the bromine attacked the trimethylamine hydrobromide part of the compound. If the first view were the correct one, such a salt should be possible with ammonium bromide. Accordingly, the ammonium salt was made and crystallized from a solution containing bromine. The original compound, $SeBr_4.2NH_4Br$, resulted. Trimethylamine hydrobromide was next crystallized from a solution containing free bromine. A new compound, having the formula $(CH_3)_3N.Br_2$, was obtained,

[1] Pogg. Ann., **125**, 325.

which dissolved in water with the liberation of the halogen.

The work on this bromine addition-product of trimethylamine led to interesting results, which are described in another part of the present paper.

It was the intention to study the series of salts formed by mono-, di-, and trimethylamine, and to observe in what way the increase in the number of methyl groups affected the compounds. The great wealth of material found and the difficulties encountered rendered the investigation of the di- and trimethylamine compounds alone possible. With these, interesting differences have been observed, but the series must be completed before any general conclusions can be drawn.

The double salts described in the following pages are tabulated below:

With Trimethylamine, $(CH_3)_3N$.

The Chlorides:

$SeOCl_2.(CH_3)_3N.HCl.$

$SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O.$

The Bromides:

$SeBr_4.SeOBr_2.2(CH_3)_3N.HBr.$

$SeBr_4.2(CH_3)_3N.HBr.$

$SeBr_4.2[(CH_3)_3N.Br_2].$

$SeBr_4.2[(CH_3)_3N.Br_2].(CH_3)_3N.HBr.$

With Dimethylamine, $(CH_3)_2HN$.

The Chlorides:

$2SeOCl_2.3(CH_3)_2HN.HCl.$

$SeO_2.(CH_3)_2NH.HCl.$

The Bromides:

$2SeBr_4.SeBr.3(CH_3)_2HN.HBr.$

$SeBr_4.2(CH_3)_2HN.HBr.$

$SeBr_4.2[(CH_3)_2HN.Br_2].$

$SeBr_4.2[(CH_3)_2HN.Br_2].(CH_3)_2HN.HBr.$

METHODS OF ANALYSIS.

Selenium.—The double salts about to be described differed markedly in their action toward water. Some dissolved to a clear solution, others gave off free bromine, and still others

went into solution with precipitation of selenium. The methods of analysis had to be varied, accordingly, to suit each particular case.

In the first part of the investigation, when the trimethylamine salts were studied, the selenium was determined gravimetrically. The salt was dissolved in water, sodium sulphite was added, and then an excess of strong hydrochloric acid. It is necessary to have the solution acid, as an excess of sodium sulphite prevents the complete precipitation of the selenium. The solution was heated to incipient boiling until the selenium sank to the bottom of the vessel as a black powder. The precipitate was filtered into a weighed Gooch crucible and dried at 90° for two hours. This method yielded excellent results, although, in most cases, the amount of selenium weighed was small.

A more rapid method was desirable and, accordingly, that devised by Muthmann and Schäfer[1] was tried. This method is based on the fact that hydriodic acid is oxidized by selenium dioxide with the liberation of iodine. The reaction is as follows:

$$SeO_2 + 4HI = Se + 2H_2O + 2I_2.$$

When the halogen compounds of selenium are treated with an excess of water, the selenium passes into the form of selenious acid. If hydriodic acid is present, four atoms of iodine will be liberated from each atom of selenium. The method of analysis is as follows: The salt is weighed into a glass-stoppered bottle of 100 cc. capacity. Potassium iodide, water, and about 1 cc. of dilute hydrochloric acid are added. There is immediate precipitation of selenium and of iodine, which goes into solution in the excess of the potassium iodide. The iodine is titrated with sodium thiosulphate, using starch paste as indicator. The precipitated selenium, which comes down as a fine red powder, renders the determination of the end-reaction difficult, and, therefore, interferes with the accuracy of the results.

An attempt to improve this method resulted in a modification which proved to be very simple and eminently satisfac-

[1] Ber. d. chem. Ges., **26**, 1008.

tory. The solution of the salt is titrated directly with sodium thiosulphate without the addition of potassium iodide. To the solution is added an excess of sodium thiosulphate and about 5 cc. of dilute hydrochloric acid. The excess is then titrated with iodine. The solution remains perfectly clear, and the first tint of blue can, therefore, be easily seen. The addition of hydrochloric acid is necessary in order to get a sharp end-reaction. The solution must be tested at the end of the titration by adding a few drops of acid. If the color does not change, the point is the one desired. If, however, the blue color deepens, sufficient acid and sodium thiosulphate have not been added in the first instance. The determination can be saved by the addition of more thiosulphate and acid until the color remains constant, and finally titrating back to color again. If hydrochloric acid equivalent to the thiosulphate is used, the above is unnecessary. The small amount of hydrochloric acid necessary does not affect the sodium thiosulphate during the short time it is in contact with it.

Four molecules of sodium thiosulphate are equivalent to one of selenium dioxide. The method was tested by making parallel standardizations of a solution of sodium thiosulphate with selenium dioxide, with a salt of known composition, and with iodine.

The results follow:

I. 0.2073 gram I required 23.30 cc. $Na_2S_2O_3$ solution.

II. 0.3061 gram I required 34.49 cc. $Na_2S_2O_3$ solution.

One atom of selenium is equivalent to four atoms of iodine, therefore,

I. 1 cc. $Na_2S_2O_3$ solution was equivalent to 1.388 mg. Se.

II. 1 cc. $Na_2S_2O_3$ solution was equivalent to 1.386 mg. Se.

III. 0.0728 gram SeO_2 required 37.27 cc. $Na_2S_2O_3$ solution.

IV. 0.0867 gram SeO_2 required 44.18 cc. $Na_2S_2O_3$ solution.

From which follows:

III. 1 cc. $Na_2S_2O_3$ solution was equivalent to 1.390 mg. Se.

IV. 1 cc. $Na_2S_2O_3$ solution was equivalent to 1.397 mg. Se.

V. 0.2015 gram salt containing 20.57 per cent. Se required 40.07 cc. $Na_2S_2O_3$.

This gives:

V. 1 cc. $Na_2S_2O_3$ solution equivalent to 1.387 mg. Se.

In the latter part of the work the standardization of the sodium thiosulphate solution was made by means of a solution of selenium dioxide of known strength.

Selenium was precipitated when some of the compounds were dissolved in water. It was necessary to determine in these cases the selenium precipitated as well as the total amount. The total selenium was determined gravimetrically as described above. That which went into solution as selenium dioxide was next determined by the volumetric method in another portion, and the precipitated selenium found by difference. This method gave better results than weighing the precipitated selenium directly, as the amount set free was usually very small.

The determination of the selenium in the compounds which gave off bromine was made gravimetrically. At first the bromine was removed by passing steam through the solution and titrating, but this method did not yield as accurate results as the gravimetric, which was accordingly used.

Halogens.—At first the gravimetric method was used for the determination of the halogens. The precipitation was made in the usual way and the precipitate filtered off while the solution was still hot, because, if allowed to cool, silver selenite crystallized out. The results came usually low when the precipitate was filtered off as soon as the solution had cleared up. It was found advisable to let the solution cool, and when the precipitate had become granular, to heat just to boiling before filtering.

The large number of analyses which had to be made rendered a quicker method desirable. The Volhard method was tested, therefore, to see if the selenium in the compounds would interfere with the accuracy of the results. When the ferric ammonium alum is added to the solution of the salt

a precipitate is formed. If slightly more dilute nitric acid than is required to clear up the solution is added, the precipitation of the halogen takes place normally and the selenium compound remains dissolved. The method was tested. A weighed quantity of potassium chloride was dissolved in water containing selenium dioxide and the chlorine determined.

I. 0.1614 gram KCl gave 0.0766 gram Cl.
II. 0.2202 gram KCl gave 0.1044 gram Cl.

	Calculated for KCl.	Found. I.	II.
Cl	47.54	47.46	47.42

As stated, some of the salts gave off free bromine when dissolved in water. It was necessary to determine both the bromine set free and the total halogens in the compounds. To find the latter, the salt was weighed into a dry beaker and a dilute solution of sulphur dioxide carefully added. As the bromine was liberated it was reduced. In this solution the hydrobromic acid was determined by titration with a solution of silver nitrate. To determine the free bromine the salt was weighed into a dry glass-stoppered bottle and potassium iodide and water added. The iodine set free was that equivalent to the bromine plus that liberated by the selenium dioxide. The latter was calculated from the percentage of selenium in the compound, and the amount equivalent to the bromine found by difference. It is necessary to add a small quantity of hydrochloric acid in order to liberate the hydriodic acid, which reacts with the selenium dioxide.

The halogen in the compounds which dissolved with precipitation of selenium was determined volumetrically in the filtered solution.

TRIMETHYLAMINE SALTS.

The Chlorides.

Salt of the Composition $SeOCl_2.(CH_3)_3N.HCl$.—Selenium tetrachloride and trimethylamine hydrochloride were brought together in strong hydrochloric acid in proportions varying from three to one of the former to one to three molecules of the lat-

ter and the solution left to crystallize in a desiccator. After standing about six weeks crystals appeared, quite pure in the solutions containing an excess of selenium, but in the other beakers mixed with trimethylamine hydrochloride. The double salt was separated mechanically and proved to be the same compound which was obtained in pure condition in the solution in which the constituents had been mixed in the proportion of two molecules of selenium tetrachloride to one of trimethylamine hydrochloride.

The salt is exceedingly soluble in water, hydrochloric acid and alcohol. It must be obtained by slow evaporation, for if an attempt is made to concentrate the solution by heat, a thick syrup is formed. The salt is insoluble in ether, but dissolves in a mixture of alcohol and ether, the solubility increasing with the amount of the former. A mixture of equal parts of alcohol and ether containing concentrated hydrochloric acid is the best solvent from which to crystallize. Notwithstanding its great solubility, it can be obtained in well-defined crystals. These are colorless, monoclinic plates, elongated in the direction of the orthodiagonal axis. A careful examination was impossible, as the salt is very hygroscopic.

Two samples were analyzed with the following results:

I. 0.3154 gram salt gave 0.0946 gram Se.

II. 0.1874 gram salt gave 0.0565 gram Se.

III. 0.2263 gram salt gave 0.3693 gram AgCl.

IV. 0.1985 gram salt gave 0.3254 gram AgCl.

	Calculated for $SeOCl_2.(CH_3)_3N.HCl$.	Found. I.	II.	III.	IV.
Se	30.23	30.00	30.15	....	....
Cl	40.64	....	....	40.36	40.55

Salt of the Composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.—Muthmann and Schäfer, working with the double salts containing selenium and ammonium, discovered that the only chloride possible was one of the composition $2SeO_2.NH_4Cl.2H_2O$. With trimethylamine hydrochloride in strong hydrochloric acid, the decomposition of the selenium tetrachloride did not go so far, for selenium oxychloride, $SeOCl_2$, entered into

combination. An attempt was according made to get a salt analogous to that made by Muthmann and Schäfer. Selenium tetrachloride and trimethylamine hydrochloride were crystallized from dilute hydrochloric acid. A mixture of two salts was obtained. In order to get the second chloride in pure condition, selenium tetrachloride and trimethylamine hydrochloride, in the proportion of two molecules of the former to one of the latter, were crystallized from a mixture of equal parts of alcohol and ether. The salt was obtained in colorless, semitransparent plates. The salt described above, $SeOCl_2.(CH_3)_3N.HCl$, was converted into the same compound by recrystallization from alcohol and ether without the presence of acid. Complete breaking down of the selenium oxychloride to selenium dioxide did not take place, one-half alone being changed. The relation between the two salts can be seen best by doubling the formula of the compound $SeOCl_2.(CH_3)_3N.HCl$.

$$SeOCl_2.SeOCl_2.2(CH_3)_3N.HCl.$$
$$SeOCl_2SeO_22(CH_3)_3N.HCl.H_2O.$$

Muthmann and Schäfer found that for each molecule of selenium dioxide there was a molecule of water present in the compound. The rule is followed here also. There is but one molecule of selenium dioxide and one of water.

Another step suggested itself, the complete breaking down of the selenium oxychloride to oxide and the formation of the salt $SeO_2(CH_3)_3N.HCl.H_2O$. An attempt was made to get this salt by crystallizing selenium dioxide and the chloride of trimethylamine from alcohol and ether. Only a small amount of salt was obtained, which proved to have the composition $SeOCl_2.SeO_2.2(CH_3)_3N.HCl.H_2O$.

In making both of the chlorides, selenium dioxide and hydrochloric acid can be used instead of the chloride. The ease of preparation and the properties of the oxide render its use more advantageous.

The analyses of the two samples of the salt follow :

I. 0.2012 gram salt gave 0.0651 gram Se.

II. 0.1565 gram salt gave 0.0508 gram Se.

III. 0.2257 gram salt gave 0.2667 gram AgCl.
IV. 0.2103 gram salt gave 0.2486 gram AgCl.

	Calculated for $SeOCl_2.SeO_2 2(CH_3)_3N.HClH_2O$.	Found. I.	II.	III.	IV.
Se	32.49	32.35	32.46	....	....
Cl	29.10	....	....	29.25	29.24

The Bromides.

A systematic search for the possible bromides was made. Selenium tetrabromide and trimethylamine hydrobromide, in varying proportions, were dissolved in hydrobromic acid and the solution evaporated to crystallization. Three different salts were formed. Special precautions were necessary to get the salts pure, as there was a great tendency for two salts to crystallize together.

Salt of the Composition $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$.—Two molecules of selenium tetrabromide and one molecule of the bromide of trimethylamine were dissolved in dilute hydrobromic acid, and the solution evaporated to crystallization. On cooling, long red needles separated. These were removed, washed with absolute alcohol, and analyzed. This salt has attractive properties. It is stable in dry air and can be recrystallized from dilute hydrobromic acid, water, and alcohol. From hot saturated solutions in acid it separates as long stout needles, sometimes 2 cm. in length. By slow evaporation, large well developed orthorhombic crystals of a deep red color were obtained. The usual habit is a combination of prism, orthopinacoid, and basal plane. At times the pyramids and the orthodomes occur. This is the most stable of the bromides containing trimethylamine and selenium, and is the form in which the two halides tend to unite unless special precautions are taken. If crystallization takes place rapidly in a solution containing an excess of trimethylamine hydrobromide, this salt crystallizes out until the solution cools, when another compound is deposited.

There is no direct method of proving the presence of both selenium tetrabromide and selenium oxybromide in the compound, but all the facts are in accord with the formula given.

The ratio of selenium to bromine is one to four. It could not, therefore, be a simple double halide containing selenium tetrabromide. And, further, recognizing the tendency of the bromide of selenium to decompose, the above formula seems justified. As is generally admitted, the constitution of the double halides is not expressed by any such formula as $SeBr_4.2NH_4Br$. Accepting the explanation of their constitution advanced by Remsen,[1] in the formula given above, the $SeOBr_2$ means simply that all of the oxygen has not been replaced by bromine. A constitutional formula of such a salt can be written.

The analysis of the compound follows:

I. 0.3141 gram salt gave 0.0529 gram Se.

II. 0.3531 gram salt gave 0.0601 gram Se.

III. 0.2246 gram salt gave 0.3616 gram AgBr.

IV. 0.3281 gram salt gave 0.5277 gram AgBr.

	Calculated for $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$.	Found. I.	II.	III.	IV.
Se	16.90	16.84	17.00	....	....
Br	68.51	....	....	68.44	68.43

Salt of the Composition $SeBr_4.2(CH_3)_3N.HBr$.—If a solution containing a large excess of trimethylamine hydrobromide in dilute hydrobromic acid is evaporated to crystallization, a dark, greenish-brown mass of fine needles mixed with the salt, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, is first deposited. If this solution is left to evaporate further in a desiccator, there appear, floating on the surface of the solution and scattered throughout the mass of green needles, large, perfectly formed red octahedra modified by cube. These can be readily separated and the salt obtained pure. This salt proved to be the compound $SeBr_4.2(CH_3)_3N.HBr$, analogous to the ammonium, potassium, and rubidium double halides with selenium bromide. These also crystallize in octrahedra. If selenium tetrabromide and trimethylamine hydrobromide, in the molecular proportions of one to two, are dissolved in dilute hydrobromic acid and the solution left to evaporate slowly, the salt is obtained generally mixed, however, with some of the green salt.

[1] Am. Chem. J., 11, 291.

It is impossible to get it from a hot saturated solution. In this respect it differs from the potassium and ammonium salts of like composition. The analysis gave the following results :

I. 0.1589 gram salt gave 0.0183 gram Se.
II. 0.2969 gram salt gave 0.0339 gram Se.
III. 0.2718 gram salt gave 0.4501 gram AgBr.
IV. 0.1299 gram salt gave 0.2150 gram AgBr.

	Calculated for $SeBr_4.2(CH_3)_3N.HBr$.	Found. I.	II.	III.	IV.
Se	11.65	11.52	11.42	....	....
Br	70.68	....	....	70.47	70.40

A third bromide was also obtained but never in pure condition. As stated above, when a solution containing selenium tetrabromide and a large excess of trimethylamine hydrobromide was evaporated, fine greenish-brown needles were obtained, mixed with the two salts described. Renewed effort failed to discover a method of getting this salt free from the other compounds. Under certain conditions the salt is very unstable, changing readily into the compound $SeBr_4.2(CH_3)_3N.HBr$. If a solution containing selenium tetrabromide and trimethylamine hydrobromide, in the proportion of one molecule of the former to three of the latter, is evaporated to crystallization, the salt crystallizes out in green needles or flakes, as long as the solution is hot. If an attempt is made to remove it, the crystals break up and change to a red powder. At times the salt was obtained in good condition after the solution had cooled to the temperature of the room. The movement of the beaker was sufficient to cause a partial change from the green needles to the red powder. An analysis of this mixture showed less bromine and more selenium than was required for the salt $SeBr_4.2(CH_3)_3N.HBr$. This was evidence that the green crystals and the red powder were not two forms of the same compound. The green needles were obtained at times in a stable form, but in this case always mixed with the other two salts. When an attempt was made to recrystallize the impure green salt from hydrobromic acid, it did not go into solution at once, but sank to the bot-

tom of the vessel as a dark brown oil, which was slowly taken up by the acid. It is hoped that further work will clear up the nature of this compound.

Salt of the composition $SeBr_4.2[(CH_3)_3N.Br_2]$.—This salt was first prepared as the result of the action of bromine on the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. The oxy-salt was treated with bromine and concentrated hydrobromic acid and heated until solution took place. On cooling, a dark-red powder crystallized out. It was hoped in this way to replace the oxygen by bromine and to thus obtain the compound $SeBr_4.(CH_3)_3N.HBr$. The crystalline precipitate did not conduct itself, however, like a double halide of selenium and trimethylamine. It dissolved in water with evolution of bromine and, on evaporation to crystallization, the double salts above described were obtained. The study of the compound led to experiments on trimethylamine hydrobromide. This took up bromine in the same way as the double salt and was converted into the compound $(CH_3)_3N.Br_2$, in which one bromine atom takes the place of hydrogen in trimethylamine hydrobromide, $(CH_3)_3N.HBr$. This evidently entered into combination with selenium tetrabromide to form a double salt. The salt can be obtained best in the following manner: Selenium tetrabromide and the bromide of trimethylamine in the molecular ratio of one to two are dissolved in dilute hydrobromic acid, and the solution evaporated till, on cooling, a salt will separate out. To the hot solution is added bromine. The salt crystallizes in well-formed, stout, needle-shaped crystals of a dark-red to greyish-black color. The surface color is like that of iodine, the powder is dark-red. The salt is very stable in dry air. It can be crystallized from hydrobromic acid containing bromine, and, if the solution is allowed to evaporate slowly, the salt is obtained in large clusters of octrahedra grouped together. It gives off two atoms of bromine quantitatively, when dissolved in water. The analyses resulted as follows:

I. 0.2447 gram salt gave 0.0230 gram Se.

II. 0.3545 gram salt gave 0.0336 gram Se.

III. 0.1770 gram salt gave 0.1352 gram Br.

IV. 0.2242 gram salt gave 0.1713 gram Br.

V. 0.3074 gram salt gave 0.2770 gram I.

VI. 0.1392 gram salt gave 0.1245 gram I.

In analyses V and VI the iodine is that liberated by the free bromine plus that set free by the selenium dioxide. Deducting the latter and finding the equivalent in bromine we have:

V. 0.3074 gram salt gave 0.0585 gram free Br.

VI. 0.1392 gram salt gave 0.0263 gram free Br.

	Calculated for $SeBr_4.2[(CH_3)_3N.Br_2]$.	Found. I.	II.	III.	IV.	V.	VI.
Se	9.44	9.39	9.48	....	....	....	....
Total Br	76.45	....	....	76.37	76.44	....	....
2 atoms Br	19.11	....	....	....	....	19.03	18.90

Salt of the composition $SeBr_4.2[(CH_3)_3N.Br_2].(CH_3)_3N.HBr$.—As a new kind of compound was obtained by crystallizing from solutions containing bromine, the effect of varying the proportions of the constituents was studied. In all cases, when the method described above was used, that is, crystallizations from hot saturated solutions, the same compound, $SeBr_4.2[CH_3)_3N.Br_2]$, was obtained. But when a solution containing a large excess of trimethylamine hydrobromide (five molecules to one of selenium tetrabromide) and bromine was allowed to crystallize slowly, a double bromide was obtained, mixed with the compound $(CH_3)_3N.Br_2$. The salt crystallizes in red crystals, which, in general appearance, resemble the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$. These are easily separated from the mixture and thus obtained in pure condition. When the salt is dissolved in water, two atoms of bromine are liberated. This shows that but two molecules of the compound $(CH_3)_3N.Br_2$ are present. The atomic ratio of selenium to bromine is one to nine. The selenium in the selenium tetrabromide requires four atoms of bromine. The two molecules of $(CH_3)_3N.Br_2$ furnish four more. A molecule of trimethylamine hydrobromide would bring the number of halogen atoms up to nine. The analysis of the compound agrees with this composition.

I. 0.2175 gram salt gave 0.0170 gram Se.
II. 0.2260 gram salt gave 0.0379 gram Br.
III. 0.2115 gram salt gave 0.3653 gram AgBr.

	Calculated for $SeBr_4.2[(CH_3)_3.N.Br_2].(CH_3)_3N.HBr$.	Found. I.	II.	III.
Se	8.06	7.81	....	....
2 atoms Br	16.37	....	16.70	....
Total Br	73.65	....	....	73.49

SALTS WITH DIMETHYLAMINE.

The Chlorides.

Salt of the composition $2SeOCl_2.3(CH_3)_2NH.HCl$.—Following the method which was used with trimethylamine hydrochloride, two double salts containing selenium and dimethylamine were obtained. The salt $2SeOCl_2.3(CH_3)_2NH.HCl$ crystallized from a solution of two molecules of selenium tetrachloride or selenium dioxide and one of dimethylamine hydrochloride in strong hydrochloric acid. The usual habit of the crystals is a combination of a monoclinic prism with the basal planes. The salt is very soluble in water, alcohol, and hydrochloric acid, and deliquesces in the air. It melts when gently heated and remains liquid for a long time. It is insoluble in ether. A mixture of three parts ether and one of alcohol was used to wash the salt in preparing it for analysis. The results of the analyses follow:

I. 0.2015 gram salt gave 0.0557 gram Se.
II. 0.2082 gram salt gave 0.0578 gram Se.
III. 0.2086 gram salt gave 0.0899 gram Cl.
IV. 0.1732 gram salt gave 0.0746 gram Cl.

	Calculated for $2SeOCl_2.3(CH_3)_2NH.HCl$.	I.	Found. II.	III.	IV.
Se	27.57	27.64	27.76	....	....
Cl	43.24	....	....	43.10	43.07

Salt of the Composition $SeO_2.(CH_3)_2NH.HCl$.—This salt was found when the compound $3SeOCl_2.2(CH_3)_2NH.HCl$ was recrystallized from a mixture of alcohol and ether. To obtain it directly 5 grams of selenium dioxide and 3.7 grams dimethylamine hydrochloride were dissolved in the smallest quantity of water, to which a few drops of dilute hydrochloric acid

were added. The solution evaporated over sulphuric acid to a thick syrup from which, after standing two months, the salt separated in stout colorless prisms. On account of its great solubility it was difficult to free it from the adhering mother-liquor. It is interesting to note that with dimethylamine a salt containing selenium dioxide is possible, while with trimethylamine such a compound does not exist. The transition to the ammonium salt, $2SeO_2.NH_4Cl.2H_2O$, is evident. The analysis follows:

I. 0.4291 gram salt gave 0.1735 gram Se.

II. 0.4140 gram salt gave 0.3144 gram AgCl.

	Calculated for $SeO_2(CH_3)_2NH.HCl$.	Found. I.	II.
Se	41.06	40.44	....
Cl	18.38	....	18.80

The Bromides.

A series of mixtures containing selenium tetrabromide and dimethylamine hydrobromide in varying proportions was made, and the resulting salts studied. The compounds differed markedly from those formed by trimethylamine. In all cases there was a considerable quantity of a salt formed which crystallized in light red needles. It was like the compound $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ in color and crystal form, but, on examination, it proved to have the formula $SeBr_4.2(CH_3)_2NH.HBr$. The analogous compound containing trimethylamine is obtained only under special conditions, while the salt $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$ is the form in which selenium tetrabromide and trimethylamine hydrobromide tend to unite. Mixed with the salt $SeBr_4.2(CH_3)_2NH.HBr$, in the beakers containing an excess of selenium halide, were well-formed, black crystals of a rhombohedral habit. This was the salt $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$. A few green needles were formed in the solutions containing an excess of dimethylamine.

Salt of the composition $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$.—This salt can be obtained in pure condition from a solution containing a large excess of selenium tetrabromide (five mole-

cules to one of dimethylamine hydrobromide) in strong hydrobromic acid. The solution is evaporated to such a concentration that, on cooling, the salt separates. Obtained in this way, the salt crystallizes in diamond-shaped plates of a dark-brown color. If dilute hydrobromic acid is used, a large amount of the salt $SeBr_4.2(CH_3)_2NH.HBr$ is formed. Water decomposes it with precipitation of selenium. When left exposed to the air, this decomposition takes place slowly, and the salt gradually becomes red.

In the compound of selenium and trimethylamine which contains the largest percentage of selenium, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, the ratio of selenium to bromine is one to four. The same ratio exists in the dimethylamine salt containing the largest amount of selenium. But the fact that it is decomposed by water with the liberation of selenium points to a different composition from that assigned to the trimethylamine salt. Some compound of selenium containing less bromine than the tetrabromide must be present, in order to have the ratio one of selenium to four of bromine. The compound Se_2Br_2 is known and, considering the instability of the tetrabromide, there is a possibility of the formation of the lower halide, and of its entering into combination to form a double salt. Further, the monobromide is decomposed by water, and selenium is precipitated and, as stated, the salt described acts in this way. The analyses for total selenium and for bromine point to the formula given to the salt. The determination of the selenium precipitated is further evidence of its correctness. When water acts on selenium monobromide the following reaction takes place :

$$2Se_2Br_2 + 2H_2O = 3Se + SeO_2 + 4HBr.$$

That is, three-fourths of the selenium is precipitated. Now, if $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$ is the correct formula for the salt under discussion (selenium monobromide is written SeBr for simplicity) then three-fourths of the selenium in the monobromide should be precipitated; that is, three-fourths of one-third or one-fourth of the total selenium. The analy-

ses show that this is the case. The following results were obtained:

I. 0.2310 gram salt gave 0.0412 gram Se.

II. 0.4102 gram salt gave 0.0724 gram Se.

III. 0.2547 gram salt gave 0.0336 gram Se as SeO_2 in solution

IV. 0.3688 gram salt gave 0.0487 gram Se as SeO_2 in solution.

V. 0.1995 gram salt gave 0.1443 gram Br.

VI. 0.2321 gram salt gave 0.1671 gram Br.

Analyses III and IV were of the selenium dioxide in solution. The difference between this selenium and the total amount gives that which was precipitated.

	Calculated for $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$.	Found. I.	II.	III.	IV.	V.	VI.
Total Se	17.75	17.84	17.65	...	...	....	....
Precipitated Se	4.44	....	....	4.54	4.53	....	....
Br	71.91	....	....	...	...	71.83	71.99

Salt of the composition $SeBr_4.2(CH_3)_2NH.HBr$.—This is the form in which the two halides tend to unite. The salt is obtained in pure condition by evaporating a mixture of one molecule of selenium bromide and two of dimethylamine hydrobromide in dilute hydrobromic acid. When this takes place slowly, bright red, prismatic needles are obtained, which are comparatively stable in the air. It is very remarkable that this salt crystallizes in a different system from all the other selenium compounds of analogous composition. The double bromides of selenium of the general formula $SeBr_4.2MBr$, namely those containing potassium, rubidium, ammonium, and trimethylamine, all crystallize in octahedra, while the dimethylamine compound crystallizes in monoclinic or triclinic prisms.

The salt was analyzed with the following results:

I. 0.2873 gram salt gave 0.0347 gram Se.

II. 0.2353 gram salt gave 0.0285 gram Se.

III. 0.3544 gram salt gave 0.6136 gram AgBr.

IV. 0.1496 gram salt gave 0.1102 gram Br.

	Calculated for $SeBr_4.2(CH_3)_2NH.HBr$.	Found. I.	II.	III.	IV.
Se	12.13	12.07	12.11	....	....
Br	73.73	....	....	73.67	73.66

A third bromide was formed crystallizing in bright green needles like the trimethylamine compound which could not be obtained in pure condition. It was obtained once in considerable quantity in beautiful crystals mixed with some fine, red needles. It was impossible to separate the two compounds mechanically, so a few drops of water were added to the beaker and the salt redissolved, with the intention of removing the green salt, as soon as it was formed. When the solution cooled, only the red salt appeared. The crystals were redissolved over and over again without removing them from the mother liquor. When the crystallization took place the results varied without any apparent rule. At times a mixture of the red and green salt was obtained, at times the pure red, but never the green alone. Finally the exact conditions were discovered, and the salt was obtained in an apparent state of purity. It can be prepared as follows: One molecule of selenium dioxide, or tetrabromide, and six of dimethylamine hydrobromide are dissolved in concentrated hydrobromic acid, and the solution evaporated at a temperature just below the boiling-point, until a salt begins to separate out on the surface of the liquid. The beaker is now set in a warm place, and left undisturbed till the solution has cooled to 60° or 70°. A large mass of fine green needles with a metallic luster will be found. These are removed to a porous plate and thus freed from the excess of acid. It is impossible to wash the compound, as it is readily decomposed with precipitation of selenium. If the crystals are not removed while the liquid is at the temperature mentioned, they will be contaminated by another salt, which appears as soon as the solution has cooled to the temperature of the room.

Analyses of samples of the salt prepared in this way gave results which agreed with one another, but not with any possible formula.

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.Br_2]$.—The salt

was obtained in the same way as the analogous trimethylamine compound. It crystallizes in dark-red needles and is best obtained from a hot saturated solution. Its appearance and properties are like those of the corresponding salt containing trimethylamine. The following analyses were made :

I. 0.1953 gram salt gave 0.1541 gram Br.
II. 0.1847 gram salt gave 0.1453 gram Br.
III. 0.2552 gram salt gave 0.0498 gram free Br.
IV. 0.2374 gram salt gave 0.0469 gram free Br.
V. 0.3196 gram salt gave 0.0314 gram Se.
VI. 0.2044 gram salt gave 0.0200 gram Se.

	Calculated for $SeBr_4.2[(CH_3)_2NH.Br_2]$.	Found. I.	II.	III.	IV.	V.	VI.
Total Br	79.11	78.90	78.67	....	....	....	....
2 atoms Br	19.78	....	....	19.52	19.78	....	....
Se	9.76	....	....	....	....	9.88	9.78

Salt of the Composition $SeBr_4.2[(CH_3)_2NH.Br_2].(CH_3)_2NH.HBr$.—A salt of this formula was obtained from a solution of one molecule of selenium tetrabromide and six of dimethylamine hydrobromide in strong hydrobromic acid. The solution was evaporated until a salt appeared on the surface of the liquid. Bromine was then added. On cooling, long prismatic crystals of a deep maroon color were deposited. The salt has a strong crystallizing force ; the prismatic faces are well developed and possess a high lustre. It is perfectly analogous in composition to the trimethylamine salt, although quite different in appearance. It will be remembered that the compounds $SeBr_4.2(CH_3)_3N.HBr$ and $SeBr_4.2[(CH_3)_3N.Br_2].(CH_3)_3N.HBr$ are obtained only by spontaneous evaporation. The dimethylamine salts of similar composition are formed with ease in hot solutions. They also crystallize in entirely different forms in different crystalline systems.

The salt gave the following figures when analyzed :

I. 0.4419 gram salt gave 0.0367 gram Se.
II. 0.3143 gram salt gave 0.0258 gram Se.
III. 0.3077 gram salt gave 0.0519 gram free Br.
IV. 0.3075 gram salt gave 0.0517 gram free Br.
V. 0.1972 gram salt gave 0.1524 gram Br.
VI. 0.2679 gram salt gave 0.2070 gram Br.

	Calculated for $SeBr_4.2[(CH_3)_2NH.Br_2](CH_3)_2NH.HBr$.	Found. I.	II.	III.	IV.	V.	VI.
Se	8.44	8.31	8.20	....	....	....	....
2 atoms Br	17.11	....	....	16.86	16.82	....	....
Total Br	77.00	....	....	....	....	77.23	77.26

Note.—Throughout the investigation the double salts were made by using selenium tetrachloride and tetrabromide, as the available supply of selenium was in these forms. It was found that selenium dioxide dissolved in the halogen acids served the purpose just as well. The oxide was made by treating selenium with concentrated nitric acid, evaporating to dryness, and subliming the residue.

Conclusion.

The double salts which have been described exhibit such complexity of structure that they cannot be rightly grouped under the class of double halides, nevertheless it is interesting to note that with one exception the number of molecules of basic halide is never in excess of the number of halogen atoms combined with the selenium. The salts thus obey Professor Remsen's law[1] and can be explained by assuming the presence of a bivalent halogen group —(Cl = Cl)—. The one exception mentioned is the compound $SeO_2.(CH_3)_2NH.HCl$. This is not a double halide at all, and, therefore, is excluded from the generalization.

[1] Am. Chem. J., II, 291.

The Action of the Halogens on the Methylamines.

INTRODUCTION.

In the introduction to the first part of this paper it has been shown how the study of the action of bromine on the salt, $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, led to the discovery of a compound which was formed by treating trimethylamine hydrobromide with bromine. An investigation of this salt was necessary in order to make clear the nature of the double halides which were formed by its union with selenium tetrabromide.

The formula $(CH_3)_3N.HBr.Br$, with which the analytical results are in close agreement, appears highly improbable, and it was suspected that the composition should be represented by the formula $(CH_3)_3N.Br_2$, its formation being due to the substitution of bromine for the hydrogen of the hydrobromide. If this view is correct, the same product should be formed by the direct addition of bromine to trimethylamine. This formation was found to take place. An analogous addition product was formed with iodine. Dimethylamine acted in the same way, but with methylamine the power to take up two halogen atoms seemed to be lost.

The work was carried only so far as it had a direct bearing on the constitution of the double salts containing selenium.

Historical.

The action of the halogens on the aliphatic amines has been frequently investigated. Raschig[1] obtained a compound of the formula $(CH_3)_2N.Br_3.2H_2O$, by treating a water solution of dimethylamine with bromine. It is a yellow precipitate, which is decomposed slowly by water. In the exper-

[1] Ber. d. chem. Ges., 8, 2249.

iments about to be described care was taken to have both the amine and the bromine free from water. In this way an entirely different compound was obtained.

The action of the halogens on the various amines or their salts in the presence of sodium hydroxide has been investigated. These experiments led to the formation of substituted amines, such as CH_3NCl_2[1], CH_3NI_2[2], and $(CH_3)_2NI$.[3]

A compound of ammonia with iodine, perfectly analogous to the ones about to be described containing dimethyl- and trimethylamine has been prepared. Seamon[4] made the compound NH_3I_2 by passing an excess of ammonia over powdered iodine. It is the only compound of the class known with ammonia. In all other compounds with ammonia there is either a partial or complete substitution of the hydrogen by halogen. The diiodide of ammonia acts in part like the analogous addition-product with trimethylamine. With water it decomposes thus :

$$2NH_3I_2 + H_2O = N + 2HI + I + NH_4I + H_2O.$$

There is a liberation of nitrogen. This does not take place with the compound $(CH_3)_3NI_2$, although iodine is set free.

The decomposition with dilute acids is perfectly analogous in both cases.

$$NH_3I_2 + HCl = NH_3.HCl + I_2,$$

and

$$(CH_3)_3N.I_2 + HCl = (CH_3)_3N.HCl + I_2.$$

Guthrie[5] prepared the same compound by treating ammonium nitrate with potassium hydroxide and iodine.

Action of Bromine on Trimethylamine.

Trimethylemine, liberated from the chloride by means of potassium hydroxide and dried by sodium hydroxide, was conducted into a Peligot tube containing bromine cooled with ice-water. As the gas was absorbed a yellow precipitate separated. This was dried on a porous plate, and the last traces

[1] Ber. d. chem. Ges., **12**, 770.
[2] Ann. Chem. (Liebig), **230**, 221.
[3] Ann. Chem. (Liebig), **230**, 223.
[4] Chem. News, **44**, 188.
[5] J. Chem. Soc. (London), 1863, 239.

of free bromine removed by allowing the salt to stand over potassium hydroxide in a desiccator. It proved to be identical with the product formed by the action of bromine on trimethylamine hydrobromide. This latter method of preparation is more convenient. To trimethylamine hydrobromide just enough concentrated hydrobromic acid is added to dissolve it when heated. One molecule of bromine for each molecule of the salt is then added and the solution heated. On cooling with ice-water the compound crystallizes out in bright yellow flakes. These can be recrystallized from absolute alcohol, when they appear as stout prismatic needles. Water instantly decomposed the salt with a liberation of half of the bromine. It is insoluble in ether.

The analysis of the precipitate formed by the action of trimethylamine on bromine gave the following results:

I. 0.2530 gram of the salt gave off 0.0921 gram Br when dissolved in water.

II. 0.2443 gram salt gave 9.1781 gram Br after the reduction of the liberated bromine by sulphur dioxide.

	Calculated for $(CH_3)_3N.Br_2$.	Found. I.	Found. II.
1 atom Br	36.63	36.40	....
Total Br	73.06	....	72.90

The salt prepared by treating trimethylamine hydrobromide with bromine was analyzed:

0.2289 gram salt gave 0.1665 gram Br.

Total bromine, 73.06; Found, 72.72.

The action of dilute acids on the compound was next studied to discover if all the halogen is liberated under these circumstances. As has been stated, the compound NH_3I_2 is decomposed by acids, and both iodine atoms are set free. The presence of acids did not effect the decomposition of the bromine addition-product with trimethylamine. But one atom of bromine was given off. Lack of time prevented a careful study of the decomposition-products of the compound. A quantity of the salt was dissolved in water and evaporated to crystallization. Trimethylamine hydrobromide was shown to be present. This was proved by treating the

residue, after the decomposition with water, with an excess of selenium tetrabromine. The salt $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, was obtained.

Action of Iodine on Trimethylamine.

Trimethylamine was passed into a solution of iodine in absolute alcohol, and in a short time a yellow precipitate appeared. This was filtered off and washed with absolute alcohol, then dried in a desiccator and analyzed. The properties of the iodide are different from those of the bromide. While the latter is decomposed by simple contact with water, the former is almost insoluble. To effect solution the water must be heated, when decomposition takes place slowly with liberation of iodine. Further, cold alcohol readily dissolves the bromide. Heat is necessary in case of the iodide, and this causes partial decomposition. In the analysis of the compound, the weighed portion was heated in a pressure-bottle on a water-bath until the salt was completely decomposed. The total iodine was determined in one sample by reducing the free iodine with sulphur dioxide. The liberated iodine in another was dissolved in potassium iodide and titrated with sodium thiosulphate. The results of the analyses follows :

I. 0.2820 gram salt gave 0.2293 gram I.
II. 0.3138 gram salt gave 0.1455 gram free I.

	Calculated for $(CH_3)_3N.I_2$.	Found. I.	II.
Total I	81.09	81.31	....
1 atom I	40.54	....	46.36

From the last analysis it is evident that the decomposition with water is different from that which the bromide undergoes. The amount of iodine set free is considerably more than one atom. This points to the formation of free hydriodic acid in the decomposition, for it was found that dilute acids liberate all of the iodine in the compound. The normal action would be the giving off of one atom of iodine, but if hydriodic acid is set free at the same time, it would act upon a part of the compound and liberate two atoms of iodine for each

molecule of acid. The iodide when first prepared is of a light yellow color. It gradually darkens and changes into a dark brown viscous fluid. A portion of the salt was treated with dilute hydrochloric acid. There was immediate decomposition with liberation of iodine. This was titrated with sodium thiosulphate with the following result:

0.5319 gram salt gave 0.4287 gram I.
Iodine found, 80.60 per cent. ; theory, 81.09.

Action of Chlorine on Trimethylamine.

Dry trimethylamine and dry chlorine were passed into a tall cylinder, the contents being protected from the air. In the first experiment, when there was an excess of trimethylamine a white solid was formed. When this was removed it was found to be very hygroscopic and had a strong odor of chlorine. An attempt was made to get an analysis of the salt, but it was without success. The conduct of the compound suggested the probability of its being analogous to the addition-product with bromine and with iodine. It was very readily decomposed by the action of moist air. Contact with water was sufficient to destroy the bromide, and the iodide was decomposed by boiling water.

In a second experiment in which there was an excess of chlorine, the trimethylamine, on entering the cylinder, burned with a brilliant flame and soot was deposited, showing a complete breaking down of the compound.

Action of Bromine on Dimethylamine.

Dimethylamine was found to take up two bromine atoms in the same way as trimethylamine. The same compound is also formed by treating dimethylamine hydrobromide with bromine. Its reactions, appearance, and properties are similar to those of the analogous compounds containing trimethylamine. The results of the analyses made follow. Analyses I and II are of the compound formed by the action of the amine on bromine. In analyses III and IV that prepared by the action of bromine on dimethylamine hydrobromide was used.

I. 0.2392 gram salt gave 0.1875 gram total Br.
II. 0.2951 gram salt gave 0.1147 gram free Br.
III. 0.1989 gram salt gave 0.1557 gram total Br.
IV. 0.2351 gram salt gave 0.0918 gram free Br.

	Calculated for $(CH_3)_2NH.Br_2$.	Found. I.	II.	III.	IV.
1 atom Br	39.02	....	38.87	....	39.10
Total Br	78.04	78.38	....	78.23	....

Compounds Containing Two Different Halogen Atoms.

When the chloride of either dimethyl- or trimethylamine is treated with bromine, a compound is formed containing both of the halogens. It is probable that there is here also a substitution of bromine for hydrogen which, with dimethylamine, would give the compound $(CH_3)_2NH.Br.Cl$. Lack of time prevented the study of these mixed compounds. The reaction does not seem to be as clean as when bromine acts on the bromides. An analysis of the product containing dimethylamine, bromine, and chlorine pointed to the formula given above, although the results do not warrant a definite statement as to the composition of the compound.

The chlorides and bromides of both dimethyl- and trimethylamine react with iodine, forming salts which give up their iodine by contact with water.

Action of Bromine and Iodine on Methylamine.

Methylamine hydrobromide was treated with bromine in the manner described in the case of trimethylamine. There was no apparent action. When the salt was freed from the excess of bromine, it was found to be the unchanged hydrobromide. When the amine was conducted into bromine, there was a rise in temperature, and a solid substance was formed. When an attempt was made to filter off this compound, there was a slight evolution of gas. The salt proved to be methylamine hydrobromide, which must have been a secondary product.

No precipitate was formed when methylamine was passed into an alcoholic solution of iodine.

BIOGRAPHICAL SKETCH.

James Flack Norris was born in Baltimore, Md., on the twentieth day of January, 1871. He attended the public schools of Baltimore and Washington, and entered the Johns Hopkins University in 1889. He received the degree of Bachelor of Arts in June, 1892. Three years have been spent in graduate work in chemistry, mineralogy, and physics, during which time he has held the positions of University Scholar and Fellow. He was assistant in the chemical laboratory of the University of Maryland during the school year 1893–94.